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Solubility Behavior of Three Aromatic Hydrocarbons in Distilled Water and Natural Seawater†

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■ The solubilities of three aromatic hydrocarbons were determined at 25 °C in natural seawater and distilled water. Saturation was achieved by equilibration of water and an excess of hydrocarbon by mechanical agitation. All three hydrocarbons, toluene, acenaphthene, and pyrene, were less soluble in seawater than in distilled water. The magnitude of the "salting out" effect increased with increasing molar volume of hydrocarbon. Temperature effects on aromatic-hydrocarbon solubility in seawater, studied at 15, 20, and 25 °C, were also directly related to molar volume. Temperature, rather than salinity, variations during toxicological studies with aqueous solutions of aromatic hydrocarbons would appear to present a greater challenge to toxicant concentration stasis, particularly so for experiments utilizing concentrations near the solubility limit.

Introduction

As part of a study designed to ascertain the effects of selected petroleum refinery effluent hydrocarbons on wild phytoplankton populations, we have determined the solubilities of three aromatic hydrocarbons in aqueous solution and 35‰ salinity natural seawater. The hydrocarbons chosen for study were toluene, acenaphthene, and pyrene, the latter two of which exhibit aqueous solubilities in the μg of solute/L range (*1*, *2*). Use of saturated hydrocarbon solutions in experiments with the algae was anticipated on the basis of earlier toxicological studies with related marine organisms (*3*). Since experimental design entailed the use of media of variable temperature and salinity, it was necessary to establish the effect of these variables on hydrocarbon solubility.

Experimental Section

Saturated solutions were generated by equilibrating water with an excess of hydrocarbon in an all-glass apparatus consisting of a 1-L Erlenmeyer flask, fitted with a ground-glass stopper and a side-arm tap which was plugged with glass wool. Flasks containing 500 mL of water and hydrocarbon were placed in a constant-temperature (±0.1 °C) gyrotary shaker (200 rpm) for at least 24 h. Following a 12-h stationary equilibration period, an aliquot (100 mL) of saturated solution was drained through the glass-wool plug and into a volumetrically calibrated separatory funnel. Acenaphthene and pyrene were isolated from solution by triplicate extraction with 10 mL of *n*-hexane, which recovered over 99% of hydrocarbon as determined in experiments with spiked solutions. Toluene was extracted by passing measured volumes through 0.6 × 6 cm columns of a superficially porous bonded C_{18} stationary-phase adsorbent (Bondapak C_{18}, Water Associates, Milford, MA), which provided better than 99% extraction efficiency for volumes of toluene solution less than 50 mL. Toluene was eluted from columns with trichlorofluoromethane (Freon-11).

Hydrocarbon levels in concentrated extracts (or eluates) were determined on a Hewlett-Packard Model 5840A gas chromatograph equipped with a flame ionization detector and an electronic integrator. Detector and inlet port temperatures were 350 and 250 °C, respectively. Two columns were employed: a ⅛ in. × 8 ft stainless-steel column of 10% TCEP on 10/120 Chromsorb for toluene analyses and a WCOT SP-2100 glass column (30 m × 0.25 mm i.d.) for acenaphthene and pyrene determinations. The oven temperature and the programming rate were variable depending on the hydrocarbon under study. Concentrations were determined by peak-area comparison with that of external standards. All values were corrected for evaporation and handling losses, as determined by use of internal-standard hydrocarbons. Hydrocarbon concentrations in extracts (or eluates) were additionally determined by peak-height comparison with standards via ultraviolet spectrophotometry on a Beckman ACTA MVI recording spectrophotometer. Agreement between gas-chromatographic and spectrometric analyses was typically within 2%.

Analytical-grade aromatic hydrocarbons were used following purification. Toluene (Burdick & Jackson, Muskegon, MI) was purified by triple distillation in glass. High-purity (99.9%) acenaphthene (Aldrich Chemical Co.) was obtained by double recrystallization from distilled methanol. Pyrene (Aldrich Chemical Co.) was separated from its major contaminant, 2,3-benzanthracene, by derivitization with 2,4,6-trinitrophenol. Water used for solubility determinations and cleaning of glassware was doubly distilled in an all-glass system and was free of trace organics. Extraction solvents were also doubly distilled in glass. Seawater collected off the Scripps pier was filtered twice through a 0.22-μm membrane and twice extracted with *n*-hexane (10:1, v/v) before use. Salinity was adjusted to 35‰ with doubly distilled water or NaCl by use of an American Optical refractive-index salinometer. All seawater blanks failed to exhibit chromatographic response after a 100-fold concentration. All glassware was rinsed with water and hexane, soaked in a dichromate–sulfuric acid bath for 6 h, rinsed with doubly distilled water, and dried at 200 °C until just before use.

Results

Table I shows solubilities of the aromatic hydrocarbons in distilled water and seawater at 25 °C. Values obtained in this work are compared with those of Eganhouse and Calder (*1*), May et al. (*2*), and Sutton and Calder (*4*). Agreement is quite good, with the exception of the acenaphthene data. This may be due, in part, to the inclusion of naphthalene in solute analyses of previous studies. Naphthalene is the major contaminant of high-purity acenaphthene, and these two hydrocarbons are not easily distinguished with conventional (noncapillary column) chromatographic equipment. All measurements give the precision as the standard deviation of the mean for six replicates.

Table II gives data demonstrating the effect of temperature on solubility of three aromatic hydrocarbons in seawater. All values represent means for six determinations. Standard deviations were ±1% or less. Since experimental temperatures during our toxicity studies (with surface seawater) were not anticipated to be significantly below 15 °C, this temperature was chosen as a lower limit (*5*).

Discussion

To explain the dissolution process, investigators have correlated certain properties of aromatic hydrocarbons with their solubilities. Molar volume and surface area have provided the

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Table I. Solubilities of Three Aromatic Hydrocarbons in Freshwater and Seawater at 25 °C

molecule	solubility in distilled water		solubility in seawater		solubility in distilled water from lit., mole fraction
	mole fraction	μg/g	mole fraction	μg/g	
toluene	5.5×10^{-6}	506.7 ± 6.1	4.5×10^{-6}	418.5 ± 5.0	5.8×10^{-6} (*4*)
acenaphthene	1.6×10^{-5}	2.42 ± 0.02	1.2×10^{-5}	1.84 ± 0.04	2.3×10^{-5} (*1*)
pyrene	6.4×10^{-10}	0.13 ± 0.01	4.6×10^{-10}	0.09 ± 0.01	6.5×10^{-10} (*2*)

most accurate correlations, particularly for a homologous series of compounds (*4, 6*). The logarithm of solubility is frequently observed to be directly correlated with molar volume. Our data for three nonhomologous aromatic hydrocarbons exhibit a linear relation between molar volume and log of solubility (Table II).

Solubility in distilled water and higher ionic strength media may be related by the Setschenow equation which empirically describes the magnitude of the "salting out effect":

$$\log (S_0/S_s) = K_s C_s \qquad (1)$$

where S_0 and S_s are concentrations of the solute in fresh and salt water, respectively, K_s is the Setschenow constant for the salt solution, and C_s is the molar salt concentration. Values of K_s calculated for the aromatic hydrocarbons investigated in this work are shown in Table III and compared to values calculated from the McDevit and Long (*9*) equation, as supplemented by Gordon and Thorne (*10, 11*). Gordon and Thorne (*10, 11*) demonstrated that the effect of sea salt upon hydrocarbon solubility is additive; that is, the value of K_s for sea salt can be calculated by knowing the values of K_s for the component salts and using the equation

$$\log S_i = \log S_i^0 - \sum_{i=1}^{n} N_i K_i C_s \qquad (2)$$

where S_i is the solubility of the hydrocarbon in salt solution. S_i^0 is the solubility of the hydrocarbon in pure water, N_i is the mole fraction of the ith salt component in sea salt, K_i is the salting parameter of the ith salt component in sea salt, C_s is the sum of the individual salt molarities, and n is the number of major salts in sea water. Agreement between observed and theoretical salting-out constants was quite good. Thus, only large changes in salinity would result in significant alterations of maximum obtainable concentrations of these aromatic hydrocarbons when dissolved in natural seawater.

Except for toluene, when the ionic strength of an aqueous solution was constant, maximal solute dissolution was strongly influenced by temperature (Table II). This conclusion was also made by Schwarz (*12*) in studies with polynuclear aromatic hydrocarbons and 0.5 M NaCl solutions. Reductions in maximal solubility due to lower temperature appear to be linearly related to enthalpy of solution, which is generally greater for hydrocarbons of greater molar volume (*13*). As seen in previous work, the solubility of toluene is little affected by temperatures in the range 15–25 °C (*14*). Data in Table II suggest that seawater solutions of different temperature will vary somewhat in their ability to solubilize aromatic hydrocarbons, particularly when nominal concentrations are near the solubility limit. These data may be useful in planning future toxicological studies with such compounds on communities in areas of the sea where different temperatures are found.

Table II. Solubilities of Three Aromatic Hydrocarbons in Seawater at Various Temperatures [a]

hydrocarbon	molar vol., mL	log solubility (μg/kg)		
		15 °C	20 °C	25 °C
toluene	109 (*6*)	5.61	5.61	5.62
acenaphthene	150 (*7*)	2.33	2.74	3.26
pyrene	172 (*8*)	1.75	1.85	1.95

[a] Salinity = 35‰, 0.5 M.

Table III. Salt Parameters for Three Aromatic Hydrocarbons at 25 °C

hydrocarbon	K_s (obsd), L/mol	K_s (calcd), L/mol
toluene	0.166	0.190
acenaphthene	0.238	0.253
pyrene	0.319	0.304

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